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(54) 【発明の名称】 1, 2-ジクロロエタンの製造方法

(57) 【要約】 (修正有)

【課題】 設備コスト及び運転コストの観点から極めて有利な1, 2-ジクロロエタンを製造する新規な方法を提供する。

【解決手段】 下記の工程を含む1, 2-ジクロロエタンの製造方法。

第一工程：塩化水素を塩素を含有するガスに変換する工程

第二工程：第一工程により得られる塩素を含有するガスを1, 2-ジクロロエタンと接触させることにより、塩素を含有する1, 2-ジクロロエタンを得る工程

第三工程：第二工程により得られる塩素を含有する1, 2-ジクロロエタン中の塩素とエチレンを反応させることにより1, 2-ジクロロエタンを得る工程。

【特許請求の範囲】

【請求項1】 下記の工程を含む1, 2-ジクロロエタンの製造方法。

第一工程：塩化水素を塩素を含有するガスに変換する工程

第二工程：第一工程により得られる塩素を含有するガスを1, 2-ジクロロエタンと接触させることにより、塩素を含有する1, 2-ジクロロエタンを得る工程

第三工程：第二工程により得られる塩素を含有する1, 2-ジクロロエタン中の塩素とエチレンを反応させることにより1, 2-ジクロロエタンを得る工程

【請求項2】 第一工程により得られる塩素を含有するガスが、塩化水素を触媒の存在下、酸素を含有するガスで酸化することにより得られたものである請求項1記載の1, 2-ジクロロエタンの製造方法。

【請求項3】 請求項1記載の各工程に加え、下記の工程を有する請求項1又は請求項2記載の1, 2-ジクロロエタンの製造方法。

第四工程：第三工程により得られる1, 2-ジクロロエタンの一部を第二工程へリサイクルして供給し、残りの1, 2-ジクロロエタンを製品として取得する工程

【請求項4】 請求項1及び請求項3記載の各工程に加え、下記の工程を有する請求項1又は請求項2記載の1, 2-ジクロロエタンの製造方法。

第五工程：第四工程により得られる製品の1, 2-ジクロロエタンを塩化ビニルと塩化水素に熱分解する工程

【請求項5】 請求項1及び請求項3及び請求項4記載の各工程に加え、下記の工程を有する請求項1又は請求項2記載の1, 2-ジクロロエタンの製造方法。

第六工程：第五工程により得られる塩化ビニルと塩化水素を分離し、塩化水素を第一工程にリサイクルして供給する工程

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、1, 2-ジクロロエタンの製造方法に関するものである。更に詳しくは、塩化水素を塩素を含有するガスに変換し、得られる塩素を含有するガスを1, 2-ジクロロエタンと接触させ、得られる塩素を含有する1, 2-ジクロロエタン中の塩素とエチレンを反応させることにより、1, 2-ジクロロエタンを製造する新規な方法であって、設備コスト及び運転コストの観点から極めて有利な1, 2-ジクロロエタンの製造方法に関するものである。

【0002】

【従来の技術】1, 2-ジクロロエタンを製造する方法としては、たとえば塩化水素と酸素とエチレンを反応させる方法が知られている。

【0003】

【発明が解決しようとする課題】かかる状況において、本発明が解決しようとする課題は、塩化水素を塩素を

含有するガスに変換し、得られる塩素を含有するガスを1, 2-ジクロロエタンと接触させ、得られる塩素を含有する1, 2-ジクロロエタン中の塩素とエチレンを反応させることにより、1, 2-ジクロロエタンを製造する新規な方法を提供する点に存するものである。

【0004】

【課題を解決するための手段】すなわち、本発明は、下記の工程を含む1, 2-ジクロロエタンの製造方法に係るものである。

第一工程：塩化水素を塩素を含有するガスに変換する工程

第二工程：第一工程により得られる塩素を含有するガスを1, 2-ジクロロエタンと接触させることにより、塩素を含有する1, 2-ジクロロエタンを得る工程

第三工程：第二工程により得られる塩素を含有する1, 2-ジクロロエタン中の塩素とエチレンを反応させることにより1, 2-ジクロロエタンを得る工程

【0005】

【発明の実施の形態】本発明において用いられる塩化水素は、塩素化合物の熱分解反応や熱分解反応、有機化合物のホスゲン化反応、脱塩化水素反応又は塩素化反応、焼却炉の燃焼反応等において発生した塩化水素を含むいかなるものを使用することができる。

【0006】本発明における第一工程とは、塩化水素を塩素を含有するガスに変換する工程である。塩化水素を塩素を含有するガスに変換する方法としては、塩化水素を触媒の存在下、空気等の酸素を含有するガスで酸化することにより塩素を含有するガスに変換する方法、塩化水素を電気分解することにより塩素を含有するガスに変換する方法をあげることができる。中でも、塩化水素を酸化ルテニウムを含有する触媒の存在下、空気等の酸素を含有するガスで酸化することにより塩素を含有するガスに変換する方法が、高収率で塩化水素を塩素に変換することができるために好ましい。

【0007】本発明における第二工程とは、第一工程により得られる塩素を含有するガスを1, 2-ジクロロエタンと接触させることにより、塩素を含有する1, 2-ジクロロエタンを得る工程である。塩素を含有するガスを1, 2-ジクロロエタンと接触させる方法としては、吸収塔を用いて接触させる方法があげられる。吸収塔内には充填物又は棚段が用いることが、接触効率を大きくする上で好ましい。塩素を含有するガスを1, 2-ジクロロエタンと接触させる温度は-50~200℃、好ましくは-10~100℃、更に好ましくは、0~100℃で行われる。該温度が-50℃よりも低い場合には、設備コストが高くなり、経済的に不利になることがあり、一方200℃よりも高い場合には、1, 2-ジクロロエタンに塩素が十分に吸収されないことがある。圧力は0.1~2MPaで行われる。該圧力が0.1MPaよりも低い場合には、1, 2-ジクロロエタンに塩素が

十分に吸収されないことがあり、一方2MPaよりも高い場合には、設備コストが高くなり、経済的に不利になることがある。1, 2-ジクロロエタンの量は、塩素を含有するガス中の塩素重量に対して0.1~200倍量、好ましくは1~100倍量、更に好ましくは、1~50倍量で実施される。1, 2-ジクロロエタンの量が過小であると、塩素が十分に吸収されないことがあり、一方1, 2-ジクロロエタンの量が過多であると、設備コストが高くなり、経済的に不利になることがある。

【0008】本発明においては、第一工程と第二工程の間に、第一工程により得られる塩素を含有するガスを、水及び/又は塩酸と接触させて、塩化水素と水を主成分とする溶液と塩素を含有するガスに分離する工程、及び/又は塩素を含有するガス中の水分を除去する工程を有することが好ましい。

【0009】本発明における第三工程とは、第二工程により得られる塩素を含有する1, 2-ジクロロエタン中の塩素とエチレンを反応させることにより1, 2-ジクロロエタンを得る工程である。1, 2-ジクロロエタン中の塩素をエチレンと反応させる反応方式としては、固定床流通方式、流動層流通方式、または、均一系流通方式をあげることができ、液相、気相両相とも実施することができる。たとえば、液相の場合、生成物1, 2-ジクロロエタン中で触媒を溶解させて実施することができる。反応圧力は、通常0.1~5MPaで実施される。反応温度は、0~500℃、好ましくは、20~300℃、更に好ましくは、20~200℃で行われる。1, 2-ジクロロエタン中の塩素をエチレンと反応させる場合には、1, 2-ジクロロエタン中の塩素に加えて別の塩素を供給することもできる。本発明においては、塩素を含有する1, 2-ジクロロエタンとエチレンを反応させて得られる反応熱（塩素1モルあたりの発熱量は180kJ）を、塩素を含有する1, 2-ジクロロエタン及び/又はエチレンの予熱、及び/又は他プロセスの熱源として熱回収することが、運転コストの抑制の観点から好ましい。たとえば、反応熱により温度上昇した反応液及び/又は反応ガスは、塩素を含有する1, 2-ジクロロエタン及び/又はエチレンを予熱することにより熱回収することができる。また、水と熱交換させてスチームを発生させたり、他プロセスの熱源として熱回収することもできる。他プロセスの熱源としては、たとえば、塩化ビニルモノマー製造プラントや、1, 2-ジクロロエタン製造プラント等における、蒸留塔のリボイラーや、反応器及び/又は分解炉の予熱等を利用することができる。

【0010】本発明における第四工程とは、第三工程により得られる1, 2-ジクロロエタンの一部を第二工程へリサイクルして供給し、残りの1, 2-ジクロロエタンを製品として取得する工程である。本発明においては、第一工程、第二工程及び第三工程に加え、第四工程

を有することが好ましい（図2）。

【0011】本発明における第五工程とは、第四工程により得られる製品の1, 2-ジクロロエタンを塩化ビニルと塩化水素に熱分解する工程である。本発明においては、第一工程、第二工程、第三工程及び第四工程に加え、第五工程を有することが好ましい（図3）。

【0012】本発明における第六工程とは、第五工程により得られる塩化ビニルと塩化水素を分離し、塩化水素を第一工程にリサイクルして供給する工程である。本発明においては、第一工程、第二工程、第三工程、第四工程及び第五工程に加え、第六工程を有することが好ましい（図4）。

【0013】

【実施例】以下、本発明を実施例により説明する。

実施例1

[]内の数字は図1に示す機器に対応し、()内の英数字は図1に示すストリームに対応する。塩化水素を塩素を含有するガスに変換する工程[1]へ、表1に示す組成の窒素、酸素、塩化水素を含有するガス(a)10.6kg/hを連続的に供給し、圧力0.6MPa、温度300℃~380℃で反応を行い、得られる反応ガスから未反応塩化水素と生成水を分離して乾燥させると、表-1に示す組成の塩素を含有するガス(b)9.2kg/hが得られる。続いて、塩素を含有するガス(b)を吸収塔[2]へ連続的に供給し、同時に1, 2-ジクロロエタン(c)100kg/hを連続的に供給し、塔頂圧力0.5MPa、塔頂温度5℃、塔底温度18℃の条件下で接触させると、塔頂部からは、表1に示す組成の未吸収ガス(d)が得られ、塔底部からは表1に示す組成の塩素を含有する1, 2-ジクロロエタン塔底液(e)が得られる。続いて、1, 2-ジクロロエタンを製造する反応器[3]へ、吸収塔[2]の塔底部から得られる塩素を含有する1, 2-ジクロロエタン塔底液(e)を連続的に供給し、同時にエチレン1.5kg/hを連続的に供給し、圧力0.3MPa、温度120℃に調節すると、塩素を含有する1, 2-ジクロロエタン塔底液(e)中の塩素が1, 2-ジクロロエタンに変換され、1, 2-ジクロロエタン(f)が得られる。各ストリームの組成を表1に示す。

【0014】

【表1】

| | <a> | | <c> | <d> | <e> | <f> |
|-------------|------|------|-----|------|------|-----|
| 成分 | | | | | | |
| 塩化水素 | 36.6 | - | - | - | - | - |
| 塩素 | - | 34.9 | - | - | 3.1 | - |
| 窒素 | 48.2 | 55.6 | - | 85.0 | - | - |
| 酸素 | 15.1 | 9.6 | - | 15.0 | - | - |
| 1,2-ジクロロエタン | - | - | >99 | - | 99.9 | >99 |

(単位：重量%)

【0015】実施例2

1 1内の数字は図3に示す機器に対応し、()内の英数字は図3に示すストリームに対応する。1, 2-ジクロロエタンのリサイクル工程14へ、実施例1と同様に得られる1, 2-ジクロロエタン(g)を連続的に供給し、一部を1, 2-ジクロロエタン(e)として吸収塔12へリサイクルすると、製品1, 2-ジク*

*クロロエタン(g)が得られる。続いて、1, 2-ジクロロエタンの熱分解反応器15へ、製品1, 2-ジクロロエタン(g)を連続的に供給すると、塩化ビニルと塩化水素(h)が得られる。各ストリームの組成を表2に示す。

【0016】

【表2】

| 成分 | <a> | | <c> | <d> | <e> | <f> | <g> | <h> |
|-------------|------|------|-----|------|-------|-----|-----|------|
| 塩化水素 | 30.0 | - | - | - | - | - | - | 30.0 |
| 塩素 | - | 34.0 | - | - | 3.1 | - | - | - |
| 窒素 | 48.2 | 66.0 | - | 86.0 | - | - | - | - |
| 酸素 | 15.1 | 0.6 | - | 16.0 | - | - | - | - |
| 1,2-ジクロロエタン | - | - | >99 | - | 100.0 | >99 | >99 | - |
| 塩化ビニル | - | - | - | - | - | - | - | 63.1 |

(単位：重量%)

【0017】

【発明の効果】以上説明したとおり、本発明により、塩化水素を塩素を含有するガスに変換し、得られる塩素を含有するガスを1, 2-ジクロロエタンと接触させ、得られる塩素を含有する1, 2-ジクロロエタン中の塩素とエチレンを反応させることにより、1, 2-ジクロロエタンを製造する新規な方法を提供することができた。

【図面の簡単な説明】

【図1】本発明のフローを示す図である。

【図2】本発明の好ましいフローを示す図である。

【図3】本発明の好ましいフローを示す図である。

【図4】本発明の好ましいフローを示す図である。

【符号の説明】

1 塩化水素を塩素を含有するガスに変換する工程

2 吸収塔

※

※3 1, 2-ジクロロエタンを製造する反応器

20 4 1, 2-ジクロロエタンのリサイクル工程

5 1, 2-ジクロロエタンの熱分解反応器

6 塩化ビニルと塩化水素を分離し、塩化水素をリサイクルする工程

a 塩化水素を含有するガス

b 塩素を含有するガス

c 1, 2-ジクロロエタン

d 未吸収ガス

e 塩素を含有する1, 2-ジクロロエタン塔底液

f 1, 2-ジクロロエタン

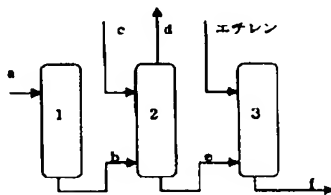
30 g 製品1, 2-ジクロロエタン

h 塩化ビニルと塩化水素

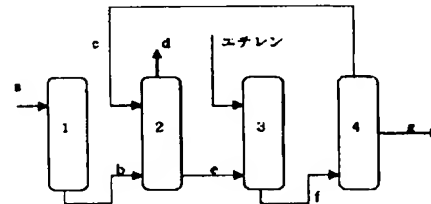
i 塩化ビニル

j 塩化水素

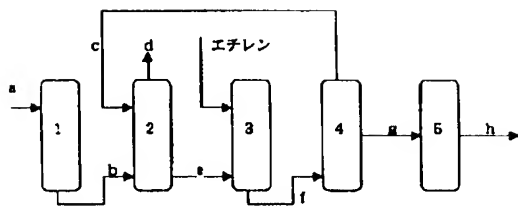
【図1】



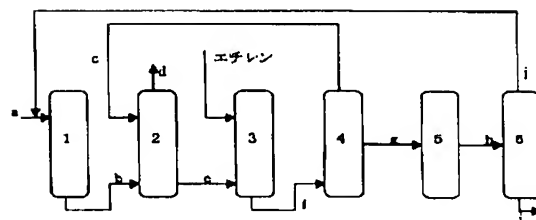
【図2】



【図3】



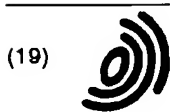
【図4】



フロントページの続き

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(54) **METHOD OF CHLORINE PURIFICATION AND PROCESS FOR PRODUCING
1,2-DICHLOROETHANE**

(57) A method for chlorine purification in which crude chlorine containing nitrogen and/or oxygen is purified to separate the nitrogen and oxygen from the chloride, characterized in that the crude chlorine containing nitrogen and/or oxygen is contacted with 1,2-dichlo-

roethane to cause the 1,2-dichloroethane to absorb the chlorine contained in the crude chlorine, and a process for producing 1,2-dichloroethane which comprises reacting ethylene with the chlorine contained in the chlorine containing 1,2-dichloroethane.

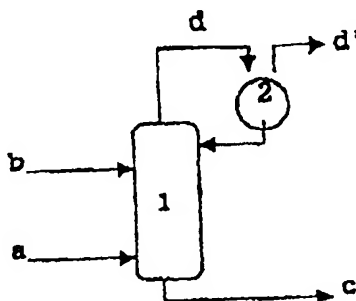


Fig. 1

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DescriptionTECHNICAL FIELD

5 [0001] The present invention relates to a method for purifying chlorine and a process for producing 1,2-dichloroethane. More particularly, the present invention relates to a method for purifying chlorine excellent in separation efficiency, which comprises separating nitrogen and/or oxygen from crude chlorine containing nitrogen and/or oxygen, and a process for producing 1,2-dichloroethane, which comprises reacting chlorine contained in 1,2-dichloroethane containing chlorine with ethylene, and both methods are extremely advantageous ones from viewpoints of installation cost and running cost.

BACKGROUND ART

15 [0002] As a method for purifying chlorine, which comprises separating nitrogen and/or oxygen from crude chlorine containing nitrogen and/or oxygen, a method for separating a liquid or gas containing chlorine as a major component and a gas containing nitrogen and/or oxygen as major components by compressing and/or cooling, is illustrated, but there are problems that not only the compressing and/or cooling requires great energy, but also the installation cost is large and separation efficiency is bad.

20 [0003] Further, as a method for producing 1,2-dichloroethane by reacting chlorine with ethylene, for example, a method of reacting chlorine with ethylene by supplying simultaneously chlorine purified by the above-mentioned method and ethylene into 1,2-dichloroethane, is known.

Disclosure of the Invention

25 [0004] An object of the present invention is to provide, in a method for purifying chlorine by separating nitrogen and/or oxygen from crude chlorine containing nitrogen and/or oxygen, a chlorine purification method which is excellent in separation efficiency and extremely advantageous from viewpoints of installation cost and running cost, namely, a method for purifying chlorine by separating nitrogen and/or oxygen from crude chlorine containing nitrogen and/or oxygen, wherein the method which comprises contacting crude chlorine containing nitrogen and/or oxygen with 1,2-dichloroethane to cause the 1,2-dichloroethane to absorb chlorine contained in the crude chlorine containing nitrogen and/or oxygen.

30 [0005] Further, another object of the present invention is to provide a method for producing 1,2-dichloroethane which is extremely advantageous from viewpoints of installation cost and running cost, namely a process for producing 1,2-dichloroethane, which comprises reacting chlorine contained in 1,2-dichloroethane containing chlorine with ethylene.

35 [0006] That is, the present invention is based on new findings that a difference of solubility to 1,2-dichloroethane between chlorine and nitrogen and/or oxygen, is large, and excellent separation efficiency, further suppression of installation cost and running cost can be attained by utilizing the difference.

40 [0007] Furthermore, other objects and advantages of the present invention will be apparent from the following descriptions.

Brief Description of the Drawings

[0008]

45 Fig. 1 shows a flow of purification of chlorine of the present invention.
Fig. 2 shows a flow of an example of production of 1,2-dichloroethane.
Figs. 3 to 8 show flows of other examples of production of 1,2-dichloroethane.

50 Explanation of symbols

[0009]

55 1. Absorbing column, 2. Cooler, 3. Reactor for producing 1,2-dichloroethane, 4. Pre-heater of 1,2-dichloroethane containing chlorine, 5. Heat exchanger for generating steam,
6. First step (step of converting hydrogen chloride into chlorine-containing gas), 7. Second step (absorbing column),
8. Third step (reactor for producing 1,2-dichloroethane),
9. Fourth step (Recycle step of 1,2-dichloroethane), 10. Fifth step (Pyrolyzer) of 1,2-dichloroethane, 11. Sixth step

(step of separating vinyl chloride and hydrogen chloride, and recycling the hydrogen chloride), a. Crude chlorine containing nitrogen and/or oxygen, b, b', 1,2-dichloroethane, c. 1,2-dichloroethane bottom liquid containing chlorine, d. Gas containing nitrogen and/or oxygen, d'. Non-condensation gas, E. Ethylene, e. 1,2-dichloroethane containing chlorine, f. Pre-heated 1,2-dichloroethane containing chlorine, g. Gas Containing hydrogen chloride, h. Gas containing chlorine, i. Unabsorbed gas, j. 1,2-dichloroethane as product, k. Vinyl chloride and hydrogen chloride, l. Vinyl chloride, m. Hydrogen chloride

10 Best Mode for Carrying out the Invention

[0010] As crude chlorine containing nitrogen and/or oxygen (herein-after, sometimes referred to simply as "crude chlorine") used in the present invention, crude chlorine further containing a gas such as argon, carbon dioxide, carbon mono oxide, or an organic compound, may be used.

15 [0011] In the present invention, as shown in Fig. 1, 1,2-dichloroethane containing chlorine as a bottom liquid(c) is obtained by contacting crude chlorine containing nitrogen and/or oxygen(a) with 1,2-dichloroethane(b) thereby to cause the 1,2-dichloroethane to absorb chlorine contained in the crude chlorine. Excellent separation efficiency, and further suppression of installation cost and running cost can be attained by this matter.

20 [0012] A contact temperature of the crude chlorine with 1,2-dichloroethane is -50 to 200°C, preferably -10 to 100°C, further preferably 0 to 100°C. When the temperature is lower than -50°C, it may become disadvantageous in economical because the installation cost becomes high. On the other hand, when higher than 200°C, chlorine may be insufficiently absorbed into 1,2-dichloroethane.

25 [0013] The contact is carried out under a pressure of 0.1 to 2 MPa. When the pressure is lower than 0.1 MPa, chlorine may be insufficiently absorbed into 1,2-dichloroethane, on the other hand, when higher than 2MPa, it may become disadvantageous in economical because the installation cost becomes high.

[0014] A used amount of 1,2-dichloroethane is usually 0.1 to 200 times by weight, preferably 1 to 100 times by weight, further preferably 1 to 50 times by weight to the amount of chlorine contained in the crude chlorine. When the amount of 1,2-dichloroethane is less than 0.1 times by weight, chlorine may be insufficiently absorbed into 1,2-dichloroethane, on the other hand, when the amount of 1,2-dichloroethane is more than 200 times by weight, it may become disadvantageous in economical because the installation cost becomes high.

30 [0015] After a 1,2-dichloroethane bottom liquid(c) of a column containing chlorine obtained by absorbing chlorine in the crude chlorine into 1,2-dichloroethane, is usually separated into chlorine and 1,3 dichloroethane, 1,2-dichloroethane can be recycled.

35 [0016] As shown in Fig. 1, a gas(d) containing nitrogen and/or oxygen not absorbed into 1,2-dichloroethane is discharged from the top of the column, but after the gas (d) is cooled with a cooler 2 to condense 1,2-dichloroethane thereby to separate from a non-condensation gas (d') for recovering 1,2-dichloroethane contained in the gas, the 1,2-dichloroethane can be recycled.

[0017] As the cooler, a heat exchanger is used, it is cooled with one stage or multi stages, and the temperature after cooled is -50 to 40°C.

40 [0018] A loss of 1,2-dichloroethane becomes smaller with lowering of the cooling temperature. It is preferable from viewpoints of safe operations of apparatuses to adjust concentrations of 1,2-dichloroethane in an absorbing column, a cooler, a drum, piping and the like out of the range of explosion.

[0019] In the present invention, it is preferable for improving contact efficiency to contact the crude chlorine with 1,2-dichloroethane using an absorbing column 1. It is more preferable for improving contact efficiency to use packing and plates in the absorbing column.

45 [0020] In the present invention, it is preferable to supply 1,2-dichloroethane to an upper part of a supply part of crude chlorine of the absorbing column.

[0021] In the present invention, it is preferable to use crude chlorine containing nitrogen and/or oxygen obtained by a catalytic oxidation and/or electrolysis of hydrogen chloride.

50 [0022] Among these, it is preferable to use crude chlorine containing nitrogen and/or oxygen obtained by oxidizing hydrogen chloride with an oxygen-containing gas in the presence of a catalyst containing ruthenium oxide.

[0023] Next, a process for producing 1,2-dichloroethane by reacting chlorine contained in 1,2-dichloroethane containing chlorine with ethylene, is described in detail.

55 [0024] In the present invention, as shown in Fig. 2, chlorine contained in 1,2-dichloroethane containing chlorine (e) is reacted with ethylene (E) in a reactor 3.

[0025] A chlorine concentration in the 1,2-dichloroethane containing chlorine is 0.01% by weight or more, preferably 0.1% by weight or more, more preferably 1% by weight or more. When the chlorine concentration is less than 0.01% by weight, it may become disadvantageous in economical because the installation costs become high. The upper

limit of the concentration is a saturated concentration thereof, and can be determined by temperature and pressure.

[0026] As a method of reacting chlorine in 1,2-dichloroethane containing chlorine with ethylene, a fixed bed flow method, fluidized bed flow method or homogeneous system flow method is given, and can be carried out in both of a liquid phase and gas phase. For example, in a case of the liquid phase, it can be carried out by dissolving a catalyst in 1,2-dichloroethane produced. It is carried out under a pressure of 0.1 to 5 MPa. It is carried out at a temperature of 0 to 500°C, preferably 20 to 300°C, more preferably 20 to 200°C.

[0027] When chlorine in 1,2-dichloroethane is reacted with ethylene, another chlorine may be fed in addition to the chlorine in 1,2-dichloroethane.

[0028] In the present invention, it is preferable from the viewpoint of suppression of running costs to conduct heat recovery of a reaction heat obtained by reacting 1,2-dichloroethane containing chlorine with ethylene (the generated heat quantity is 180 kJ per 1 mol of chlorine) as heat resources for pre-heating of 1,2-dichloroethane containing chlorine and/or ethylene, or for another process.

[0029] For example, heat recovery can be attained by pre-heating 1,2-dichloroethane containing chlorine and/or ethylene with a reaction liquid and/or reaction gas of which the temperature has been raised by the reaction (Fig. 3).

[0030] Further, it is possible to generate steam by a heat exchange with water and to recover the heat as a heat resource for another process (Fig. 4). As a heat resource for another process, for example, it can be utilized for pre-heating of a re-boiler, reactor and/or cracker in a vinyl chloride production plant or a 1,2-dichloroethane production plant.

[0031] In the present invention, it is preferable on points of raw material and installation costs that 1,2-dichloroethane containing chlorine is one obtained by contacting crude chlorine containing nitrogen and/or oxygen above-mentioned with 1,2-dichloroethane. Further, it is preferable that 1,2-dichloroethane is one obtained by reacting chlorine contained in 1,2-dichloroethane containing chlorine with ethylene.

[0032] Furthermore, another embodiment of 1,2-dichloroethane production is described using Fig. 5.

[0033] First, in the first step 6, hydrogen chloride in a hydrogen chloride-containing gas (g) is converted into a chlorine-containing gas (h). As hydrogen chloride, any hydrogen chloride-containing gas generated by pyrolysis of a chlorine compound, a reaction with phosgene, de-hydrogen chloride reaction or chlorination of an organic compound, or combustion in an incinerator, can be used.

[0034] As methods of converting hydrogen chloride into chlorine, there are listed a method of converting into a chlorine-containing gas by oxidizing hydrogen chloride with an oxygen-containing gas such as air in the presence of a catalyst and a method of converting into a chlorine-containing gas by electrolysis of hydrogen chloride. In these, a method of converting into a chlorine-containing gas by oxidizing hydrogen chloride with an oxygen-containing gas in the presence of a catalyst containing ruthenium oxide, is preferable because it can convert hydrogen chloride into chlorine at high yield.

[0035] Subsequently, in the second step 7, 1,2-dichloroethane containing chlorine (c) is obtained by contacting a chlorine-containing gas (h) obtained in the first step 6 with 1,2-dichloroethane thereby absorbing chlorine into 1,2-dichloroethane. The production of 1,2-dichloroethane is that as described above. In addition, gas not absorbed is discharged from the top of the column.

[0036] Further, it is preferable to set up, between the first step 6 and second step 7, a step of separating into a solution containing hydrogen chloride and water as main components, and a gas containing chlorine, by contacting a chlorine-containing gas (h) obtained in the first step 6 with water and/or hydrochloric acid, and/or a step of removing water in the chlorine-containing gas.

[0037] In the third step 8, 1,2-dichloroethane (b') is obtained by reacting chlorine contained in 1,2-dichloroethane containing chlorine (c) obtained in the second step 7 with ethylene.

[0038] The method of reacting chlorine in 1,2-dichloroethane containing chlorine (c) with ethylene is as described above.

[0039] Moreover, in the embodiment of the present invention, it is preferable to set up a fourth step 9 in addition to the first, second and third steps (Fig. 6).

[0040] The fourth step 9 is a step for feeding a part of 1,2-dichloroethane obtained in the third step 8 into the second step 7 for recycling, and getting the remained 1,2-dichloroethane as product (j).

[0041] Furthermore, in Fig. 7, a step (fifth step 10) of obtaining vinyl chloride and hydrogen chloride (k) by pyrolysis of 1,2-dichloroethane as product (j) obtained in the fourth step 9, is added, and there is an advantage that recycle of hydrogen chloride produced by pyrolysis is possible in addition to advantages described above.

[0042] Moreover, in Fig. 8, as a sixth step 11, a step of separating (k) obtained in the fifth step 10 into vinyl chloride (l) and hydrogen chloride (m), and feeding hydrogen chloride (m) into the first step 6 for recycling, is added. According to this process, a process for producing vinyl chloride; containing the purification step of chlorine containing contacting of the chlorine-containing gas with 1,2-dichloroethane as described above and the step of producing 1,2-dichloroethane by reacting chlorine in 1,2-dichloroethane containing chlorine with ethylene; and further using hydrogen chloride as a starting material which can be recycled, can be also preferably provided.

5 Example 1

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| | a | b | c | d' |
|---------------------|------|------|-------|------|
| Components | | | | |
| Chlorine | 34.0 | - | 6.3 | 1.0 |
| Nitrogen | 56.7 | - | 0.1 | 84.2 |
| Oxygen | 9.3 | - | < 0.1 | 14.0 |
| 1,2-dichloroethane | - | > 99 | 93.6 | 0.8 |
| (Unit: % by weight) | | | | |

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Example 5

[0050] As shown by a flow of Fig. 5, when, into the sixth step of converting hydrogen chloride into chlorine-containing gas, 10.6 kg/hr of a gas (g) containing nitrogen, oxygen and hydrogen chloride having a composition shown in Table 2 is continuously fed to carry out a reaction under a pressure of 0.6 MPa at a temperature of 300 to 380°C in the presence of a catalyst under a conversion of 85%, and unreacted hydrogen chloride and water produced from the obtained gas is separated and dried, 9.2 kg/hr of chlorine-containing gas (h) having a composition shown in Table 2 is obtained. Subsequently, when chlorine-containing gas (h) is continuously fed into an absorbing column 7, simultaneously, 100 kg/hr of 1,2-dichloroethane (b) is continuously fed to contact them under conditions of a pressure of the top of the column of 0.5 MPa, a temperature of the top of the column of 5°C, a temperature of the bottom of the column of 18°C, a gas (l) not absorbed having a composition shown in Table 2 is obtained from the top of the column, and 1,2-dichloroethane (c) containing chlorine having a composition shown in Table 2 is obtained as a bottom liquid. Subsequently, when, into a reactor 8 for producing 1,2-dichloroethane, the bottom liquid of 1,2-dichloroethane (c) containing chlorine obtained from the bottom of the absorbing column 7 is continuously fed, simultaneously, 1.5 kg/hr of ethylene (E) is continuously fed, and conditions are adjusted at a pressure of 0.3 MPa and temperature of 120°C, chlorine in the bottom liquid of 1,2-dichloroethane (c) containing chlorine, is converted into 1,2-dichloroethane to obtain 1,2-dichloroethane (b'). A composition of each of streams is shown in Table 2.

Table 2

| | g | h | b | l | c | b' |
|--------------------|------|------|-----|------|------|-----|
| Component | | | | | | |
| Hydrogen chloride | 36.8 | - | - | - | - | - |
| Chlorine | - | 34.9 | - | - | 3.1 | - |
| Nitrogen | 48.2 | 55.6 | - | 85.0 | - | - |
| Oxygen | 15.1 | 9.6 | - | 15.0 | - | - |
| 1,2-dichloroethane | - | - | >99 | - | 96.9 | >99 |

Example 6

[0051] As shown by a flow of Fig. 7, when 1,2-dichloroethane (b') obtained by the same method as in Example 5 is continuously fed into the step 9 of recycle of 1,2-dichloroethane and a part of them is recycled to an absorbing column 7 as 1,2-dichloroethane (b), 1,2-dichloroethane as product (j) is obtained. Subsequently, when 1,2-dichloroethane as product (j) is continuously fed into a pyrolyzer of 1,2-dichloroethane 10, vinyl chloride and hydrogen chloride (k) is obtained. A composition of each of streams is shown in Table 3.

Table 3

| | g | h | b | l | c | b' | j | k |
|---------------------|------|------|-----|------|------|-----|-----|------|
| Component | | | | | | | | |
| Hydrogen chloride | 36.6 | - | - | - | - | - | - | 36.9 |
| Chlorine | - | 34.9 | - | - | 3.1 | - | - | - |
| Nitrogen | 48.2 | 55.6 | - | 85.0 | - | - | - | - |
| Oxygen | 15.1 | 9.6 | - | 15.0 | - | - | - | - |
| 1,2-dichloroethane | - | - | >99 | - | 96.9 | >99 | >99 | - |
| Vinyl chloride | - | - | - | - | - | - | - | 63.1 |
| (Unit: % by weight) | | | | | | | | |

INDUSTRIAL APPLICABILITY

[0052] As described above, according to the present invention, there can be provided, in a method for purifying chlorine by separating nitrogen and/or oxygen from crude chlorine containing nitrogen and/or oxygen, a method for purifying chlorine, which comprises contacting crude chlorine containing nitrogen and/or oxygen with 1,2-dichloroethane thereby allowing to absorb chlorine in crude chlorine; and a method for producing 1,2-dichloroethane, which comprises reacting chlorine in 1,2-dichloroethane containing chlorine with ethylene. In addition, these methods can be used as a step in vinyl chloride production in which hydrogen chloride is used as a starting material which is capable of recycling.

Claims

1. A method for purifying chlorine which comprises separating nitrogen and/or oxygen from crude chlorine containing nitrogen and/or oxygen, wherein the method comprising contacting the crude chlorine containing nitrogen and/or oxygen with 1,2-dichloroethane thereby allowing to absorb chlorine in the crude chlorine containing nitrogen and/or oxygen into 1,2-dichloroethane.
2. The method for purifying chlorine according to claim 1, which comprises feeding the crude chlorine containing nitrogen and/or oxygen and 1,2-dichloroethane into an absorbing column to contact them.
3. The method for purifying chlorine according to claim 2, wherein 1,2-dichloroethane is supplied to an upper part of a supply part of the absorbing column to which the crude chlorine containing nitrogen and/or oxygen is supplied.
4. The method for purifying chlorine according to claim 2, wherein the crude chlorine containing nitrogen and/or oxygen is one obtained by catalytic oxidation and/or electrolysis of hydrogen chloride.
5. A process for producing 1,2-dichloroethane, which comprise reacting chlorine in 1,2-dichloroethane containing chlorine with ethylene.
6. The process for producing 1,2-dichloroethane according to claim 5, which further comprises a step of heat recovery in which a reaction liquid and/or reaction gas of which the temperature has been raised by heat obtained by reaction of chlorine in 1,2-dichloroethane containing chlorine with ethylene is used for pre-heating 1,2-dichloroethane containing chlorine and/or ethylene, and/or as a heat resource for another process.
7. The process for producing 1,2-dichloroethane according to claim 5, wherein the 1,2-dichloroethane containing chlorine is one obtained by contacting the crude chlorine containing nitrogen and/or oxygen with 1,2-dichloroethane.
8. The process for producing 1,2-dichloroethane according to claim 5, wherein 1,2-dichloroethane used for allowing to contain chlorine is one obtained by reacting chlorine in 1,2-dichloroethane containing chlorine with ethylene.
9. A process for producing 1,2-dichloroethane, which comprises the following steps:
 - first step; a step of converting hydrogen chloride into a gas containing chlorine,
 - second step; a step of obtaining 1,2-dichloroethane containing chlorine by contacting the gas containing chlorine obtained in the first step with 1,2-dichloroethane, and
 - third step; a step of obtaining 1,2-dichloroethane by reacting chlorine in the 1,2-dichloroethane containing chlorine obtained in the second step with ethylene.
10. The process for producing 1,2-dichloroethane according to claim 9, wherein the gas containing chlorine obtained in the first step is one obtained by oxidizing hydrogen chloride with a oxygen-containing gas in the presence of a catalyst.
11. The process for producing 1,2-dichloroethane according to claim 9 or 10, which further comprises the following step:
 - fourth step; a step of feeding a part of 1,2-dichloroethane obtained in the third step into the second step for recycling, and getting the remained 1,2-dichloroethane as a product.
12. The process for producing 1,2-dichloroethane according to claim 11, which further comprises the following step:
 - fifth step; a step of pyrolyzing 1,2-dichloroethane as a product obtained in the fourth step into vinyl chloride and hydrogen chloride.
13. The process for producing 1,2-dichloroethane according to claim 12, which further comprises the following step:
 - sixth step; a step of separating vinyl chloride and hydrogen chloride obtained in the fifth step, then recycling the hydrogen chloride into the first step.

Amended claims under Art. 19.1 PCT

- 5 1. A method for purifying chlorine which comprises separating nitrogen and/or oxygen from crude chlorine containing nitrogen and/or oxygen, wherein the method comprising contacting the crude chlorine containing nitrogen and/or oxygen with 1,2-dichloroethane thereby allowing to absorb chlorine in the crude chlorine containing nitrogen and/or oxygen into 1,2-dichloroethane
- 10 2. The method for purifying chlorine according to claim 1, which comprises feeding the crude chlorine containing nitrogen and/or oxygen and 1,2-dichloroethane into an absorbing column to contact them.
- 15 3. The method for purifying chlorine according to claim 2, wherein 1,2-dichloroethane is supplied to an upper part of a supply part of the absorbing column to which the crude chlorine containing nitrogen and/or oxygen is supplied.
- 20 4. The method for purifying chlorine according to claim 2, wherein the crude chlorine containing nitrogen and/or oxygen is one obtained by catalytic oxidation and/or electrolysis of hydrogen chloride.
- 25 5. (Amended) A process for producing 1,2-dichloroethane, which comprise:
 - contacting crude chlorine containing nitrogen and/or oxygen with 1,2-dichloroethane thereby making chlorine in the crude chlorine containing nitrogen and/or oxygen to absorb in the 1,2-dichloroethane and separating nitrogen and/or oxygen from the crude chlorine containing nitrogen and/or oxygen, and then
 - reacting the chlorine in the 1,2-dichloroethane with ethylene.
- 30 6. The process for producing 1,2-dichloroethane according to claim 5, which further comprises a step of heat recovery in which a reaction liquid and/or reaction gas of which the temperature has been raised by heat obtained by reaction of chlorine in 1,2-dichloroethane containing chlorine with ethylene is used for pre-heating 1,2-dichloroethane containing chlorine and/or ethylene, and/or as a heat resource for another process.
- 35 7. (Canceled)
- 40 8. The process for producing 1,2-dichloroethane according to claim 5, wherein 1,2-dichloroethane used for allowing to contain chlorine is one obtained by reacting chlorine in 1,2-dichloroethane containing chlorine with ethylene.
- 45 9. (Amended) A process for producing 1,2-dichloroethane, which comprises the following steps:
 - first step; a step of obtaining crude chlorine containing nitrogen and/or oxygen by subjecting hydrogen chloride to electrolysis and/or catalytic oxidation,
 - second step; a step of obtaining 1,2-dichloroethane containing chlorine by contacting the crude chlorine containing nitrogen and/or oxygen with 1,2-dichloroethane thereby making chlorine in the crude chlorine containing nitrogen and/or oxygen to absorb in the 1,2-dichloroethane and separating nitrogen and/or oxygen from the crude chlorine containing nitrogen and/or oxygen, and
 - third step; a step of obtaining 1,2-dichloroethane by reacting chlorine in the 1,2-dichloroethane containing chlorine obtained in the second step with ethylene.
- 50 10. (Amended) The process for producing 1,2-dichloroethane according to claim 9, wherein the crude chlorine obtained in the first step is one obtained by oxidizing hydrogen chloride with a oxygen-containing gas in the presence of a catalyst.
- 55 11. The process for producing 1,2-dichloroethane according to claim 9 or 10, which further comprises the following step:
 - fourth step; a step of feeding a part of 1,2-dichloroethane obtained in the third step into the second step for recycling, and getting the remained 1,2-dichloroethane as a product.
- 60 12. The process for producing 1,2-dichloroethane according to claim 11, which further comprises the following step:
 - fifth step; a step of pyrolyzing 1,2-dichloroethane as a product obtained in the fourth step into vinyl chloride and hydrogen chloride.

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13. The process for producing 1,2-dichloroethane according to claim 12, which further comprises the following step:

Sixth step; a step of separating vinyl chloride and hydrogen chloride obtained in the fifth step, then recycling the hydrogen chloride into the first step.

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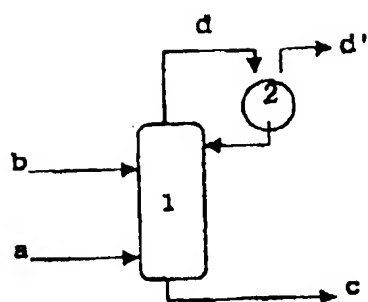


Fig. 1

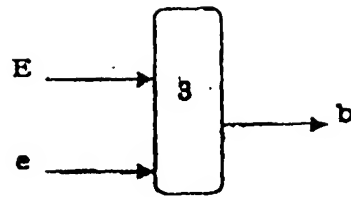


Fig. 2

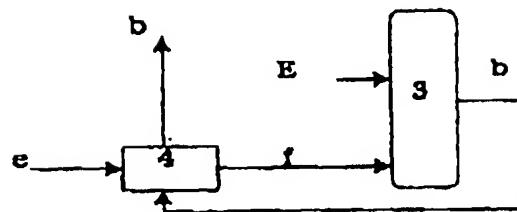


Fig. 3

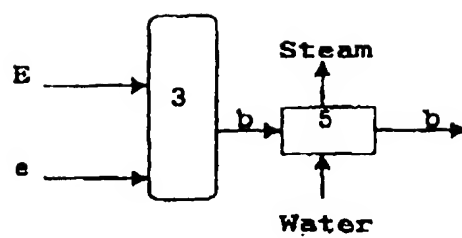


Fig. 4

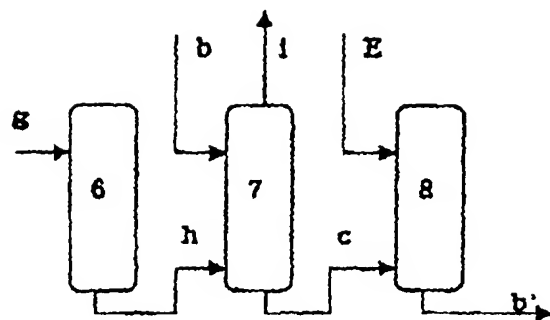


Fig. 5

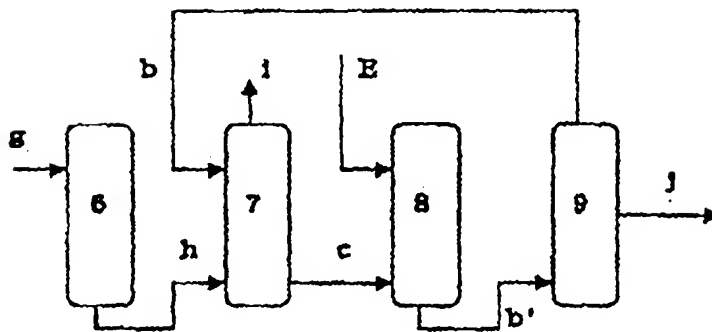


Fig. 6

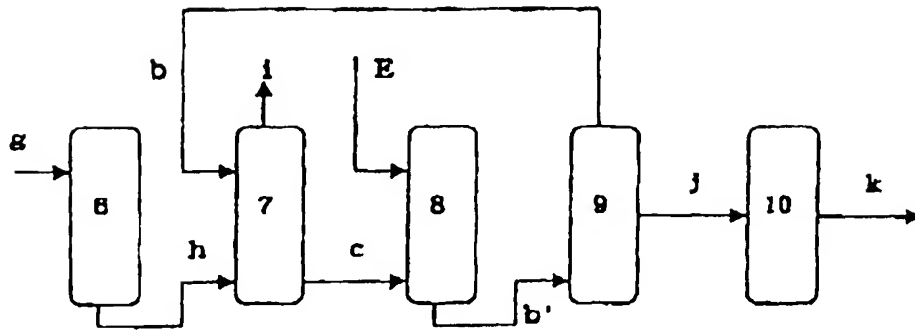


Fig. 7

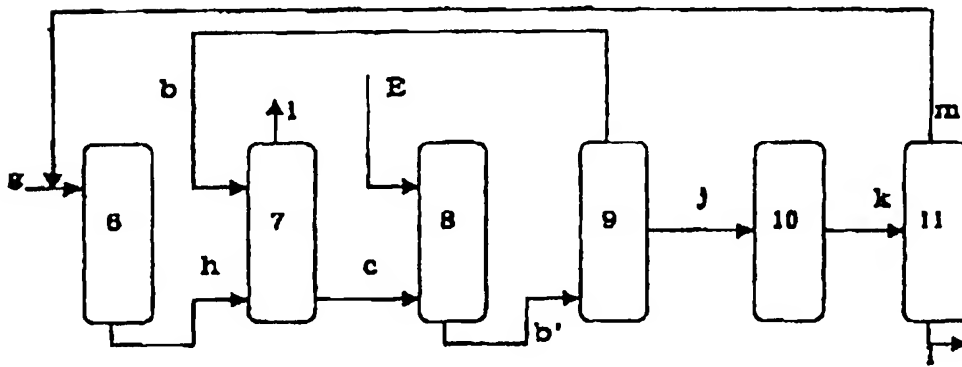


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/06172

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁷ C01B7/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁷ C01B7/00-7/24, C07C17/08, C07C19/045

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

| | | | |
|---------------------------|-----------|----------------------------|-----------|
| Jitsuyo Shinan Koho | 1926-1996 | Toroku Jitsuyo Shinan Koho | 1994-2002 |
| Kokai Jitsuyo Shinan Koho | 1971-2002 | Jitsuyo Shinan Toroku Koho | 1996-2002 |

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | US 4554392 A (Dynamit Nobel AG), 19 November, 1985 (19.11.85), Claims; column 1, lines 19 to 12; column 2, line 30 to column 4, line 17; examples; drawings & JP 60-200825 A (Dynamit Nobel AG), 24 June, 1985 (24.06.85), Claims; page 2, upper right column, lines 7 to 10; page 3, upper right column, line 7 to page 4, lower left column, line 12; examples; drawings & EP 142016 A | 5-13 |
| A | JP 58-208104 A (Mitsui Toatsu Chemicals, Inc.), 03 December, 1983 (03.12.83), Claims; page 2, lower left column, lines 13 to 15; examples; Fig. 1 (Family: none) | 1-4 |

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | JP 02-137704 A (Toagosei Co., Ltd.), 28 May, 1990 (28.05.90), Claims; examples; Fig. 1 (Family: none) | 1-4 |
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